Solutions - Chapter 16

14. First balance the redox equation;

Given; $MnO_4^- + Mo^{3+} = Mn^{2+} + MoO_2^{2+}$

MnO_4^- reduces, Mo^{3+} oxidizes. Inspection of the resulting species prompts the need for H^+ ions, the half reactions are

$$MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O \qquad (1)$$

$$2H_2O + Mo^{3+} = MoO_2^{2+} + 4H^+ + 3e \qquad (2)$$

overall: 3(1) + 5(2)

$$3MnO_4^- + 5Mo^{3+} + 4H+ = 3Mn^{2+} + 5MoO_2^{2+} + 2H_2O$$

Titration data: $V_{Mo} := 25.00$ $V_{MnO4\_blank} := 0.04$

$V_{MnO4} := 16.43$

$M_{MnO4} := 0.01033$

From the stoichiometry: $$\frac{V_{Mo} \cdot M_{Mo}}{V_{MnO4} \cdot M_{MnO4} - V_{MnO4\_blank} \cdot M_{MnO4}} = \frac{5}{3}$$

has solution(s)

$$M_{Mo} := \frac{5}{(3 \cdot V_{Mo})} \cdot \left(V_{MnO4} \cdot M_{MnO4} - V_{MnO4\_blank} \cdot M_{MnO4}\right)$$

$$M_{Mo} = 0.011$$

17. The overall reaction is between permanganate and oxalate, the half reactions are;

$$MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O \qquad (1)$$

$$C_2O_4^{-2} = 2CO_2 + 2e \qquad (2)$$

overall; $2MnO_4^- + 16H^+ + 5C_2O_4^{-2} = 2Mn^{+2} + 8H_2O + 10CO_2$

Using the stoichiometry with;

$V_{MnO4} := 18.04$ $M_{MnO4} := 0.006363$ $V_{La} := 50.00$

$$\frac{V_{MnO4} \cdot M_{MnO4}}{mole_{oxalate}} = \frac{2}{5}$$

$$mole_{oxalate} := \frac{5}{2} \cdot V_{MnO4} \cdot M_{MnO4} \qquad mole_{oxalate} = 0.287$$

Because every three oxalate ions are associated with two La ions,

$$mole_{La} := \frac{2}{3} \cdot mole_{oxalate}$$

$$M_{La} := \frac{mole_{La}}{V_{La}} \qquad M_{La} = 3.826 \times 10^{-3}$$

19. Total ml of Ce(IV) added ..; $V_{Ce} := 50.00$ $M_{Ce} := 0.1186$

Volume of Fe(II) (ml) for back titration ..; $V_{Fe} := 31.13$ $M_{Fe} := 0.04289$

$$2Ce^{4+} + NO_2^- + H_2O = 2Ce3^+ + NO_3^- + 2H^+$$

$$Ce^{4+} + Fe^{+2} = Ce3^+ + Fe^{+3}$$

Because Fe(II) vs Ce(IV) reaction is a 1:1 reaction, the leftover Ce(IV) after the reaction with nitrite ion and mmoles of Ce(IV) reacted with nitrite are;

$$mmoleCe_{excess} := V_{Fe} \cdot M_{Fe}$$

$$mmoleCe_{reacted} := V_{Ce} \cdot M_{Ce} - mmoleCe_{excess}$$

Ce(IV) : nitrite = 2:1 from the stoichiometry, for the 25.00 ml of the sample (of a 500ml solution)

$$\frac{mmoleCe_{reacted}}{mmoleNO2_{reacted}} = \frac{2}{1}$$

$$mmoleNO2_{reacted} := \frac{1}{2} \cdot mmoleCe_{reacted}$$

$$mass_{NaNO2} := mmoleNO2_{reacted} \cdot 10^{-3} \cdot 68.995$$

In 500ml the total sample was dissolved.

$$\%mass_{NaNO2} := \frac{mass_{NaNO2} \cdot \frac{500}{25}}{4.030} \cdot 100 \qquad \%mass_{NaNO2} = 78.665$$

33. Al(III) is precipitated quantitatively as Al(oxine)$_3$(s) **(Al:oxine = 1:3)**.

Redissolved ppt. to generate oxine and was eventually reacted with excess bromine (made in situ by reacting bromide with bromate in acidic conditions) oxine: bromine = 1:2.

Bromine is produced from bromate - **Bromate:Br2 = 1:3**

Excess bromine was reduced with iodide, this reaction produces iodine. **Br_2:I_2 = 1:1**

I_2 reacts with $S_2O_3^{-2}$ quantitatively (iodine:thiosulfate = 1:2);

$$I_2 + 2S_2O_3^{-2} = S_4O_6^{-2} + 2I^-$$

$V_{S2O3} := 8.83$ $M_{S2O3} := 0.05113$

mmoles of bromine generated by bromate,bromide rxn $mmolesadded_{Br2} := 3 \cdot 25.00 \cdot 0.0200$

mmoles of iodine reacted at the final stage;

$$\frac{mmoles_{I2}}{V_{S2O3} \cdot M_{S2O3}} = \frac{1}{2} \qquad mmoles_{I2} := \frac{1}{2} \cdot V_{S2O3} \cdot M_{S2O3}$$

Using the stoichiometries given above unreacted (excess) bromine;

$mmolesBr2_{excess} := mmoles_{I2}$

mmoles of bromine consumed for the oxine reaction

$mmoles_{Br2} := mmolesadded_{Br2} - mmolesBr2_{excess}$

Also;

$$mmoles_{oxine} := \frac{1}{2} \cdot mmoles_{Br2}$$

$$mmoles_{Al} := \frac{1}{3} \cdot mmoles_{oxine}$$

$mgmass_{Al} := mmoles_{Al} \cdot 26.981$ $mgmass_{Al} = 5.73$